ASSIGNING STATES IN THE JAHN-TELLER COUPLED INFRARED SPECTRA OF CH_3O AND CD_3O

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The ground $\tilde{X}^2E$ vibrations of the methoxy radical have intrigued both experimentalists and theorists alike due to the presence of a conical intersection at the C_{3v} molecular geometry. This conical intersection causes methoxy's vibrational spectrum to be strongly influenced by Jahn-Teller coupling, this leading to large amplitude vibrations and extensive mixing of the two lowest electronic states. This coupling combined with spin-orbit and Fermi couplings greatly complicates the assignments of states. In this talk we describe our efforts to assign the states of both CH_3O and CD_3O.

Using the potential energy force field and calculated spectra of Nagesh and Sibert[1] as a starting point, vibrational mixing is considered using various zero-order representations. When the zero-order states are the diabatic normal mode states, there is sufficient mode mixing that the normal mode quantum numbers are no longer good labels. The mixing of the zero-order states can be reduced by including additional terms in the zero-order Hamiltonian, H^o. We consider the choice of including the first order Jahn-Teller coupling between one of the three degenerate normal modes. As the rocking motion has the largest Jahn-Teller coupling, this is the coupling that is included in H^o. Although the normal mode quantum numbers of the rocking basis functions are no longer good quantum numbers, due to the Jahn-Teller induced vibronic mixing, the zero-order states can be labeled with the linear Jahn-Teller quantum numbers.[2] This work extends these ideas by considering an H^o that includes linear Jahn-Teller coupling between *two* sets of degenerate vibrations. Plots of the resulting zero-order states are presented, and the spectral transitions recently observed[3] for both CH_3O and CD_3O in a p-H_2 matrix are assigned using these basis functions. The extent of state-mixing found for the full Hamiltonian H for various choices of H^o is illustrated via the use of correlation diagrams obtained by plotting the eigenvalues of $H^o + \delta(H - H^o)$ as a function of δ where δ varies from zero to one.

[1] Nagesh, J.; Sibert, E. L. *J. Phys. Chem. A* **2012**, *116*, 3846–3855.

[2] Barckholtz, T. A.; Miller, T. A. *Int. Revs. in Phys. Chem.* **1998**, *17*, 435–524.

[3] Yu-Fang Lee, Wei-Te Chou, and Yuan-Pern Lee (private communication).